

THE CLAIMSWHAT IS CLAIMED IS:

54. 1. A semiconductor wafer cleaning formulation, comprising the following components in the percentage by weight ranges shown, based on the total weight of such components:

	fluoride source	1-21%
5	organic amine(s)	
	20-55%	
	a nitrogenous component, selected from nitrogen-containing	
	carboxylic acids and imines	0.5-40%
	water	23-50%
10	metal chelating agent(s)	0-21%
	TOTAL	100%

2. The cleaning formulation of claim 1 wherein said fluoride source comprises a fluoride species selected from the group consisting of:

15 ammonium fluoride; and  
triethanolammonium fluoride (TEAF).

3. The cleaning formulation of claim 1 wherein said organic amine(s) comprise an amine selected from the group consisting of:

diglycolamine (DGA),  
methyldiethanolamine (MDEA),

pentamethyldiethylenetriamine (PMDETA),  
triethanolamine (TEA), and  
triethylenediamine (TEDA).

4. The cleaning formulation of claim 1 wherein said nitrogenous component comprises a species selected from the group consisting of:

iminodiacetic acid (IDA);  
glycine;  
nitrilotriacetic acid (NTA); and  
1,1,3,3-tetramethylguanidine (TMG).

5. The cleaning formulation of claim 1 including at least one metal chelating agent selected from the group consisting of:

acetoacetamide,  
ammonium carbamate,  
ammonium pyrrolidinedithiocarbamate (APDC),  
dimethyl malonate,  
methyl acetoacetate,  
N-methyl acetoacetamide,  
2,4-pentanedione,  
tetramethylammonium thiobenzoate,  
tetramethylammonium trifluoroacetate, and  
tetramethylthiuram disulfide (TMTDS).

6. The cleaning formulation of claim 1 wherein said fluoride source comprises a species selected from the group consisting of:

ammonium fluoride,  
triethanolammonium fluoride (TEAF),  
5 diglycolammonium fluoride (DGAF),  
tetramethylammonium fluoride (TMAF), and  
triethylamine tris (hydrogen fluoride) (TREAT-HF).

7. The cleaning formulation of claim 1 wherein said organic amine(s) comprises an amine selected from the group consisting of:

10 diglycolamine (DGA),  
methyldiethanolamine (MDEA),  
pentamethyldiethylenetriamine (PMDETA),  
triethanolamine (TEA),  
triethylenediamine (TEDA),  
15 hexamethylenetetramine,  
3, 3-iminobis (N,N-dimethylpropylamine), and  
monoethanolamine.

8. The cleaning formulation of claim 1, wherein said nitrogenous component comprises a species from the group consisting of:

iminodiacetic acid (IDA)  
glycine  
nitrilotriacetic acid (NTA)

1,1,3,3-tetramethylguanidine (TMG)

$\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$

$\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$

$\text{CH}_3\text{C}(=\text{NH})\text{CH}_2\text{C}(\text{O})\text{CH}_3$

$(\text{CH}_3\text{CH}_2)_2\text{NC}(=\text{NH})\text{N}(\text{CH}_3\text{CH}_2)_2$

$\text{HOOCCH}_2\text{N}(\text{CH}_3)_2$

$\text{HOOCCH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$

9. The cleaning formulation of claim 1 wherein said fluoride source comprises a species selected from the group consisting of:

Ammonium fluoride,

triethanolammonium fluoride (TEAF),

diglycolammonium fluoride (DGAF),

tetramethylammonium fluoride (TMAF), and

triethylamine tris (hydrogen fluoride) (TREAT-HF);

said organic amine(s) comprise a species selected from the group consisting of:

diglycolamine (DGA),

methyldiethanolamine (MDEA),

pentamethyldiethylenetriamine (PMDETA),

triethanolamine (TEA),

triethylenediamine (TEDA),

hexamethylenetetramine,

3, 3'-iminobis (N,N-dimethylpropylamine), and

monoethanolamine;

said nitrogenous component comprises a species selected from the group consisting of:

iminodiacetic acid (IDA)

glycine

nitrilotriacetic acid (NTA)

1,1,3,3-tetramethylguanidine (TMG)

and said formulation includes a metal chelating agent comprising a species selected from the group consisting of:

acetoacetamide,

ammonium carbamate,

5 ammonium pyrrolidinedithiocarbamate (APDC),

dimethyl malonate,

methyl acetoacetate,

N-methyl acetoacetamide,

2,4-pentanedione,

10 tetramethylammonium thiobenzoate,

tetramethylammonium trifluoroacetate, and

tetramethylthiuram disulfide (TMTDS).

10. The cleaning formulation of claim 1 wherein said fluoride source comprises a compound having the general formula  $R_1R_2R_3R_4NF$  in which each of the R groups is independently selected from hydrogen atoms and aliphatic groups, and wherein said formulation includes a metal chelating agent of the formula:

X-CHR-Y, in which

R is either hydrogen or an aliphatic group and

20 X and Y are functional groups containing multiply bonded moieties having electron-withdrawing properties.

11. The cleaning formulation of claim 10 wherein each of X and Y is independently selected from CONH<sub>2</sub>, CONHR', CN, NO<sub>2</sub>, SOR', and SO<sub>2</sub>Z in which R' is alkyl and Z is hydrogen, halo, or alkyl.

12. The cleaning formulation of claim 1 wherein said fluoride source comprises a compound having the formula R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>NF in which each of the R groups is hydrogen or aliphatic, and wherein said  
5 formulation includes a metal chelating agent of the formula, R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>N<sup>+</sup>O<sub>2</sub>CCF<sub>3</sub> in which each of the R groups is independently hydrogen or aliphatic.

13. The cleaning formulation of claim 1, wherein said nitrogenous component includes a compound having the formula:

10



wherein each of R and R' is independently selected from the group consisting of hydrogen, alkyl, aryl, and carboxylic acids.

14. A method for fabricating a semiconductor wafer, comprising:

15

plasma etching a metalized layer from a surface of the wafer;

plasma ashing a resist from the surface of the wafer;

cleaning the wafer by contacting same with a cleaning formulation, comprising the following components in the percentage by weight ranges shown, based on the total weight of such components:

20

fluoride source	1-21%
organic amine(s)	20-55%
a nitrogenous component, selected from nitrogen-containing carboxylic acids and imines	0.5-40%

water	23-50%
metal chelating agent(s)	0-21%
TOTAL	100%

5      15. The method of claim 14 wherein said fluoride source comprises a fluoride species selected from the group consisting of:

ammonium fluoride; and  
triethanolammonium fluoride (TEAF).

10      16. The method of claim 14 wherein said organic amine(s) comprise an amine selected from the group consisting of:

diglycolamine (DGA),  
methyldiethanolamine (MDEA),  
pentamethyldiethylenetriamine (PMDETA),  
triethanolamine (TEA), and  
15      triethylenediamine (TEDA)

17. The method of claim 14 wherein said nitrogenous component comprises a species selected from the group consisting of:

iminodiacetic acid (IDA);  
glycine;  
nitrilotriacetic acid (NTA); and  
1,1,3,3-tetramethylguanidine (TMG).

18. The method of claim 14 including at least one metal chelating agent selected from the group consisting of:

acetoacetamide,  
ammonium carbamate,  
5 ammonium pyrrolidinedithiocarbamate (APDC),  
dimethyl malonate,  
methyl acetoacetate,  
N-methyl acetoacetamide,  
2,4-pentanedione,  
10 tetramethylammonium thiobenzoate,  
tetramethylammonium trifluoroacetate, and  
tetramethylthiuram disulfide (TMTDS).

19. The method of claim 14 wherein said fluoride source comprises a species selected from the group consisting of:

15 ammonium fluoride,  
triethanolammonium fluoride (TEAF),  
diglycolammonium fluoride (DGAF),  
tetramethylammonium fluoride (TMAF), and  
triethylamine tris (hydrogen fluoride) (TREAT-HF).

20 20. The method of claim 14 wherein said organic amine(s) comprises an amine selected from the group consisting of:

diglycolamine (DGA),  
methyldiethanolamine (MDEA),



pentamethyldiethylenetriamine (PMDETA),  
 triethanolamine (TEA),  
 triethylenediamine (TEDA),  
 hexamethylenetetramine,  
 5 3, 3-iminobis (N,N-dimethylpropylamine), and  
 monoethanolamine.

21. The method of claim 14, wherein said nitrogenous component comprises a species from the group consisting of:

iminodiacetic acid (IDA)  
 glycine  
 nitrilotriacetic acid (NTA)  
 1,1,3,-tetramethylguanidine (TMG)  
 $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$   
 $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$   
 $\text{CH}_3\text{C}(=\text{NH})\text{CH}_2\text{C}(\text{O})\text{CH}_3$   
 $(\text{CH}_3\text{CH}_2)_2\text{NC}(=\text{NH})\text{N}(\text{CH}_3\text{CH}_2)_2$   
 $\text{HOOCCH}_2\text{N}(\text{CH}_3)_2$   
 $\text{HOOCCH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$

22. The method of claim 14 wherein said fluoride source comprises a species selected from the group consisting of:

10 ammonium fluoride,  
 triethanolammonium fluoride (TEAF),

diglycolammonium fluoride (DGAF),  
 tetramethylammonium fluoride (TMAF), and  
 triethylamine tris (hydrogen fluoride) (TREAT-HF);

said organic amine(s) comprise a species selected from the group consisting of:

- 5        diglycolamine (DGA),  
          methyldiethanolamine (MDEA),  
          pentamethyldiethylenetriamine (PMDETA),  
          triethanolamine (TEA),  
          triethylenediamine (TEDA),  
 10        hexamethylenetetramine,  
          3, 3-iminobis (N,N-dimethylpropylamine), and  
          monoethanolamine;

said nitrogenous component comprises a species selected from the group consisting of:

iminodiacetic acid (IDA)  
 glycine  
 nitrilotriacetic acid (NTA)  
 1,1,3,3-tetramethylguanidine (TMG)

and said formulation includes a metal chelating agent comprising a species selected from the group consisting of:

- 15        acetoacetamide,  
          ammonium carbamate,  
          ammonium pyrrolidinedithiocarbamate (APDC),  
          dimethyl malonate,  
          methyl acetoacetate,  
 20        N-methyl acetoacetamide,

2,4-pentanedione,

tetramethylammonium thiobenzoate,

tetramethylammonium trifluoroacetate, and

tetramethylthiuram disulfide (TMTDS).

- 5 23. The method of claim 14 wherein said fluoride source comprises a compound having the general formula  $R_1R_2R_3R_4NF$  in which each of the R groups is independently selected from hydrogen atoms and aliphatic groups, and wherein said formulation includes a metal chelating agent of the formula:

X-CHR-Y, in which

- 10 R is either hydrogen or an aliphatic group and

X and Y are functional groups containing multiply bonded moieties having electron-withdrawing properties.

- 15 24. The method of claim 23 wherein each of X and Y is independently selected from  $CONH_2$ ,  $CONHR'$ ,  $CN$ ,  $NO_2$ ,  $SOR'$ , and  $SO_2Z$  in which  $R'$  is alkyl and Z is hydrogen, halo, or alkyl.

25. The method of claim 14 wherein said fluoride source comprises a compound having the formula  $R_1R_2R_3R_4NF$  in which each of the R groups is hydrogen or aliphatic, and wherein said formulation includes a metal chelating agent of the formula,  $R_1R_2R_3R_4N^+O_2CCF_3$  in which each of the R groups is independently hydrogen or aliphatic.

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26. The method of claim 14, wherein said nitrogenous component includes a compound having the formula:

$COOH-CH_2-NRR'$

wherein each of R and R' is independently selected from the group consisting of hydrogen, alkyl, aryl, and carboxylic acids.

27. A method for fabricating a semiconductor wafer including the steps comprising:

5 plasma etching a metalized layer from a surface of the wafer;

plasma ashing a resist from the surface of the wafer;

cleaning the wafer by contacting same with a cleaning formulation, comprising the following components in the percentage by weight ranges shown, based on the total weight of such components:

10	a fluoride source;	1-21%
	at least one organic amine;	20-55%
	a nitrogen-containing carboxylic acid or imine	0.5-40%
	water;	23-50%
	<u>at least one metal chelating agent</u>	<u>0-21%</u>
15	TOTAL	100%

28. The method of claim 27 wherein said fluoride source is chosen from the group consisting of:

ammonium fluoride; and

triethanolammonium fluoride (TEAF).

20 29. The method of claim 27 wherein said organic amine is chose from the group consisting of:

diglycolamine (DGA),

methyldiethanolamine (MDEA),

pentamethyldiethylenetriamine (PMDETA),

triethanolamine (TEA), and

triethylenediamine (TEDA).

30. The method of claim 27 wherein said nitrogen-containing carboxylic acid or imine is selected from the group consisting of:

iminodiacetic acid (IDA)

glycine

nitrilotriacetic acid (NTA)

1,1,3,3-tetramethylguanidine (TMG)

31. The method of claim 27 wherein said metal chelating agent is selected from the group consisting of:

acetoacetamide,

ammonium carbamate,

ammonium pyrrolidinedithiocarbamate (APDC),

dimethyl malonate,

methyl acetoacetate,

N-methyl acetoacetamide,

2,4-pentanedione,

tetramethylammonium thiobenzoate,

tetramethylammonium trifluoroacetate, and

tetramethylthiuram disulfide (TMTDS).

32. The method of claim 27 wherein said fluoride source is selected from the group consisting of:

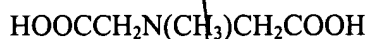
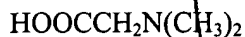
ammonium fluoride,  
 triethanolammonium fluoride (TEAF),  
 diglycolammonium fluoride (DGAF),  
 tetramethylammonium fluoride (TMAF), and  
 triethylamine tris (hydrogen fluoride) (TREAT-HF).

33. The method of claim 27 wherein said organic amine is selected from the group consisting of:

diglycolamine (DGA),  
 methyldiethanolamine (MDEA),  
 pentamethyldiethylenetriamine (PMDETA),  
 triethanolamine (TEA),  
 triethylenediamine (TEDA),  
 hexamethylenetetramine,  
 3, 3-iminobis (N,N-dimethylpropylamine), and  
 monoethanolamine.

34. The method of claim 27, wherein said nitrogen-containing carboxyl acid or imine is selected from the group consisting of:

iminodiacetic acid (IDA)  
 glycine  
 nitrilotriacetic acid (NTA)  
 1,1,3,-tetramethylguanidine (TMG)  
 $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$   
 $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$



35. The method of claim 27 wherein said fluoride source is selected from the group consisting of:

ammonium fluoride,

triethanolammonium fluoride (TEAF),

diglycolammonium fluoride (DGAF),

tetramethylammonium fluoride (TMAF), and

triethylamine tris (hydrogen fluoride) (TREAT-HF);

said organic amine is chosen from the group consisting of:

diglycolamine (DGA),

methyldiethanolamine (MDEA),

pentamethyldiethylenetriamine (PMDETA),

triethanolamine (TEA),

triethylenediamine (TEDA),

hexamethylenetetramine,

3, 3-iminobis (N,N-dimethylpropylamine), and

monoethanolamine;

said nitrogen-containing carboxylic acid or imine is chosen from the group consisting of:

iminodiacetic acid (IDA)

glycine

nitrilotriacetic acid (NTA)

1,1,3,3-tetramethylguanidine (TMG)

and said metal chelating agent is selected from the group consisting of:

acetoacetamide,  
 ammonium carbamate,  
 ammonium pyrrolidinedithiocarbamate (APDC),  
 5 dimethyl malonate,  
 methyl acetoacetate,  
 N-methyl acetoacetamide,  
 2,4-pentanedione,  
 tetramethylammonium thiobenzoate,  
 10 tetramethylammonium trifluoroacetate, and  
 tetramethylthiuram disulfide (TMTDS).

36. The method of claim 27 wherein said fluoride source comprises a compound having the formula  $R_1R_2R_3R_4NF$  in which each of the R groups is hydrogen atoms or aliphatic, and wherein said metal chelating agent has the formula:

15 X-CHR-Y, in which

R is either hydrogen or an aliphatic group, and

X and Y are functional groups containing multiply-bonded moieties having electron-withdrawing properties.

20 37. The method of claim 27 wherein said fluoride source comprises a compound having the formula  $R_1R_2R_3R_4NF$  in which each of the R groups is hydrogen or aliphatic, and wherein said metal chelating agent has the formula,  $R_1R_2R_3R_4N^+ \cdot C_2CCF_3$  in which each of the R groups is hydrogen or aliphatic.



38. The method of claim 27, wherein said nitrogen-containing carboxylic acid has the formula:



wherein each of R and R' is independently selected from the group consisting of hydrogen, alkyl, aryl, and carboxylic acid.

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39. A method of removing residue from a wafer following a resist plasma ashing step on said wafer, comprising contacting the wafer with a cleaning formulation, including (i) a fluoride source, (ii) at least one organic amine, (iii) a nitrogen-containing carboxylic acid or an imine, (iv) water, and optionally at least one metal chelating agent.

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40. A wafer cleaning formulation, including (i) a fluoride source, (ii) at least one organic amine, (iii) a nitrogen-containing carboxylic acid or an imine, (iv) water, and optionally at least one metal chelating agent.

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